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FEATURES OF FORMATION OF THE CONTACT ZONE IN THE GLAZE – CERAMICS SYSTEM

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The features of formation of the contact zone in the glaze – ceramics system in relation to the time-temperature parameters of the heat treatment are considered. The distribution of the cations Si^{4+} , Ca^{2+} , Zr^{4+} , and Al^{3+} in the opacified glaze coating and the ceramic substrate is studied. It is found that diffusion processes proceed due to viscous flow of the glaze glass.

Formation of coatings is a complex multistage process that includes sintering of glass particles and their spreading over the surface of the ceramic base. The authors of [1] distinguish five stages in coating formation. In the first stage, the layer is compacted due to rearrangement of the particles without substantial modification of their shape. The degree of compaction depends on the particle shape and the regularity and density of their packing. The second state is characterized by spheroidization of the particles, their fusion, and the spreading of the initial monolayer over the substrate. Rearrangement and separation of the glaze coating into zones continues in this stage. The coating thickness, the height of the irregularities, and the porosity inside the zones decrease; however, the layer remains unsealed and permeated by channels. The third stage is the sealing of the coating: the pore channels are disconnected and form closed cavities, and the coat loses permeability. The fourth stage is the development of the porous structure, which is manifested primarily in spheroidization of the cavities. The fifth stage is smoothing of the surface within the zones and merging of the zones. The latter depends on the wetting ability of the glass melt with respect to the ceramic substrate.

Glaze and ceramics are complicated heterophase systems that differ in their physicochemical properties and degree of structural ordering, and when they are in contact at high temperatures, a certain interaction takes place between them. This can be cation self-diffusion, mass transfer by viscous flow of the glaze melt and the softened vitreous phase of the ceramics, chemical reaction between the melt and the crystalline phases, and formation of new compounds [2].

Properties and defects of glaze coatings had been discussed earlier without taking into consideration the effect of the ceramic substrate on them. At present the structure, properties, and quality of coatings are often considered in the

context of their relationship with the ceramics. A number of significant transformations take place in the glaze coating within the temperature interval of the unmelted glaze. The glaze layer releases mechanically and chemically bound moisture, organic impurities burn out, the shrinkage increases, and the adhesive forces change. The tendency to reduce the free energy is manifested in consolidation of the glaze layer. Whereas the adhesion of the glaze to the ceramic mixture in heating occurs on the surface, starting from the moment of cooling, dissolution of the crock components and gas emission occur. The quality of a glazed article depends to a certain extent on good adhesion of the glaze to the ceramic mixture.

The study [3] notes the presence of two areas of the contact zone: a diffusion zone, i.e., a vitreous area where the dissolved ceramic mixture has penetrated into the glaze by diffusion, and a metamorphic zone, i.e., fully or partly vitrified ceramic mixture. The geometric characteristics of the indicated zones fluctuate over wide ranges and depend on many factors.

Diffusion processes, as a consequence of which an intermediate layer is formed, take place in the crystalline substance – vitreous phase – melt system. Each component has a different diffusion coefficient and a different process activation energy. The lowest diffusion coefficient and the highest activation energy are exhibited by the crystalline component, which has an ordered structure and a high bond strength at the crystal lattice points. Diffusion is a thermally activated process, and a high temperature and a long hold are required for diffusion to develop in crystalline substances [4].

Vitreous bodies have a less compact and looser structure than crystalline bodies. Atomic (ionic) diffusion in them obeys the laws established for crystalline bodies; however it proceeds more easily [5]. As the composition of the glass is changed, the number of ions participating in the diffusion

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process and their mobility change. The diffusion activation energy depends on the structural state of the glass. The diffusion entropy of a glass lattice is negative. It is found that the diffusion increases when the glass experiences tensile forces that can arise when a certain difference exists in the TCLE of the system components. Thus, the diffusion processes in the glass – ceramics system proceed primarily due to the glass.

Upon melting of a substance, the lattice energy and the activation energy needed for migration of atoms (ions) are both decreased. The melt structure is random, with the individual coordination of each atom or small ionic groups varying with time. This causes a high diffusion coefficient and a low process activation energy. Direct measurements show that the diffusion coefficient of the melt is higher than that of the solid body, and their ratio reaches values of 10^5 . The diffusion coefficients in ionic melts, to which a glaze melt belongs, are several orders of magnitude higher than in crystalline oxides or other high-melting compounds. The mobility of ions in a melt depends on their concentration, ionic radius, atomic weight, and charge. The mobility of alkali cations in silicate melts is an order of magnitude higher than the mobility of other ions. The diffusion coefficient of Ca^{2+} cations is an order of magnitude higher than that of Si^{4+} ions [4, 5].

A study of the processes taking place in the contact layer between the glaze coating and the ceramic was carried out on a Cameca MS-46 electronic probe (France). A method of linear scanning in the direction perpendicular to the glaze coating with recording of concentration curves of component distribution was used. The scanning was performed using a microanalyzer probe (probe diameter 1.5 μm , $U = 20$ kV) with recording on a pulse potentiometer tape. The experimental samples were ceramic tiles used at the Keramin Company (Minsk) with applied glaze coatings (compositions 13 and 14). The content of oxides of the considered elements in the glaze and the ceramic mixture is shown in Table 1.

The fusing temperature was 950, 1000, and 1050°C with a constant hold of 15 min. In order to determine the effect of the duration of the hold, samples were held at a constant temperature of 950°C for 15, 30, and 60 min. The variation in the time and temperature parameters is dictated by resemblance to accelerated and lengthy firing regimes for ceramic articles. The distribution of the ions Al^{3+} , Ca^{2+} , Si^{4+} , and Zr^{4+} was investigated in the glaze – ceramics contact zone. In addition to that, a microscopic analysis of the studied portion of

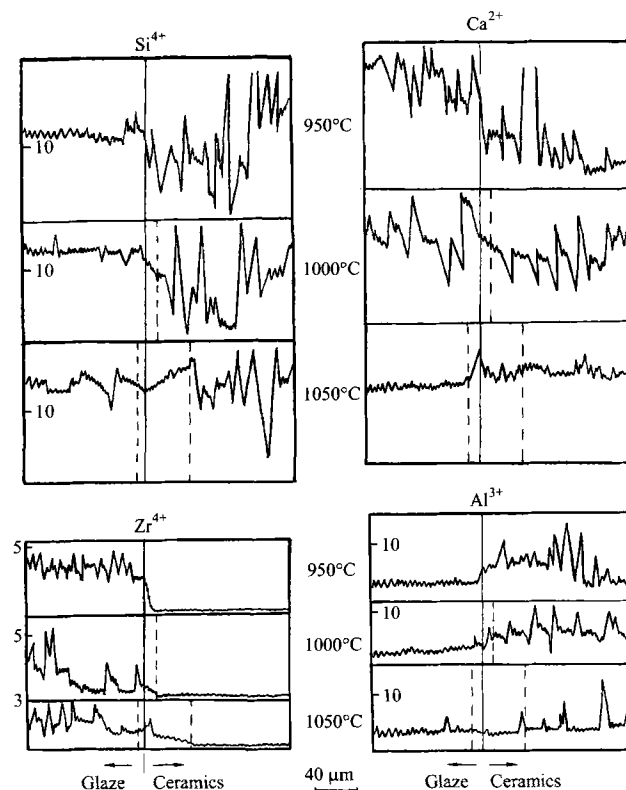


Fig. 1. Cation distribution in the glaze – ceramics system versus firing temperature.

the section was carried out using an MeF-3 metallographic microscope (Switzerland).

The cation distribution in the glaze – ceramics contact zone in relation to the fusion temperature for glaze 14 is presented in Fig. 1. The dashed lines formally indicate the contact zone in the glaze – ceramics system. Photographs of the contact zones are shown in Fig. 2.

At a heat-treatment temperature of 950°C, the glaze is separated from the ceramic by a clearly expressed interface in the form of a straight line. A photomicrograph and a spectrogram reveal an extremely inhomogeneous structure for the ceramic substrate. Thus, the curve of the silicon cation distribution exhibits intense peaks that characterize a substantial quantitative jump in this cation and troughs pointing to a very low content or virtual absence of this cation.

This is due to the fact that in the first case the microanalyzer beam passes through a quartz grain, and in the se-

TABLE 1

Composition	Content, %							
	SiO_2		Al_2O_3		CaO		ZrO_2	
	molar	weight	molar	weight	molar	weight	molar	weight
Glaze:								
13	55.00	49.00	7.50	11.40	10.50	8.80	4.00	7.30
14	55.00	50.30	5.00	7.80	10.50	8.90	4.00	7.47
Ceramic mixture	66.82	60.46	11.65	17.89	7.73	6.53	—	—

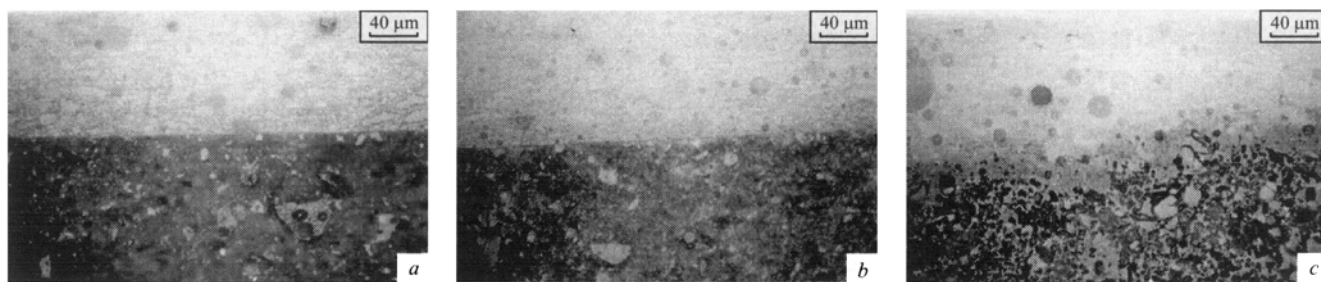


Fig. 2. Formation of the contact zone in the glaze – ceramics system in heat treatment (firing duration 15 min): *a, b, c*) firing temperature 950, 1000, and 1050°C, respectively.

cond case through a carbonate or other inclusion free of silica. This becomes obvious in correlating the concentration curves of silicon and calcium: an increase in the intensity of the Ca^{2+} concentration corresponds to a trough in the spectrogram of Si^{4+} . If the electron probe passes through a pore, a trough is observed on all concentration curves of the studied cations. The average values of the silicon concentration are typical of a dehydrated argillaceous substance or existing vitreous-phase interlayers containing approximately equal amounts of silica.

The spread in the concentration values of the Al^{3+} cation in the ceramics is significantly less than that of Ca^{2+} and Si^{4+} , which points to a more uniform distribution of it in the ceramics and the absence of an independent crystalline phase with a high concentration of Al^{3+} .

The concentration distribution curve of the Zr^{4+} cation in the ceramic substrate passes along the zero mark, since ZrO_2 is not a component of the ceramic, and under the given time-temperature conditions Zr^{4+} does not migrate from the glaze to the ceramic.

The obtained concentration distribution curves of the cations Ca^{2+} , Al^{3+} , and Si^{4+} agree with the structural features of the studied ceramics. The structure of the ceramic tile that had undergone accelerated firing at a low temperature (1000 – 1020°C) and, accordingly, is porous can be represented as a combination of quartz grains with a dehydrated argillaceous substance and crystals of impurity phases. The crystalline components are cemented by a vitreous phase of a complicated composition, the amount of which is insufficient for filling the pores. As a result, the open porosity of the ceramic remains within the range of 25 – 30%. The inhomogeneity of the ceramic structure is confirmed by the photomicrographs of the contact-zone sections (see Fig. 2), which clearly exhibit single fragmentary quartz crystals (size 20 – 40 μm), interlayers of an amorphous substance, fine lime inclusions, and crystals of impurity phases. An x-ray analysis of the ceramic substrate yields similar information.

As can be seen from Fig. 1, the distribution of the cations Si^{4+} and Al^{3+} in the glaze layer is more uniform than in the ceramic substrate, which is due to the more homogeneous structure of the vitreous glaze. It melts almost completely at a temperature of 950°C, which significantly increases the

cation diffusion coefficient and decreases the activation energy of this process. The intensity of the concentration peaks correlates with the atomic content of the elements in the glaze and the ceramic.

The distribution of the cations Zr^{4+} and Ca^{2+} in the glaze layer is less uniform, which is probably related to the limited solubility of zirconium in the melt, the presence of liquation phenomena, and the formation of crystalline phases containing these elements. Upon separation of zirconium- and calcium-containing phases, the amount of Zr^{4+} and Ca^{2+} in the vitreous phase decreases, and troughs are observed on the concentration curves.

There are virtually no differences in the distribution of the elements over the glaze coating volume. A sharp concentration transition is observed for all the elements on the glaze–ceramics contact surface, which is caused by different chemical compositions of the contiguous materials and indicates the absence of a reaction zone between the glaze and the ceramic substrate. Here virtually no intermediate layer is formed. A low temperature (950°C) and a short hold (15 min) are probably insufficient for the development of such diffusion processes as self-diffusion of cations and mass transfer via viscous flow of the melt, which agrees with the data in [6].

The photographs also record bubble chains issuing from the ceramic substrate. The presence of such bubbles can be caused [7] by vortex flows entraining them from open pores into the glaze layer. Single larger bubbles appear at the interface. Vortex flows, transferring gas bubbles to the fire-mirror surface, produce defects of the glaze coating surface (pinholes). The gas composition of the bubbles existing inside the glaze coating varies depending on the gas medium in firing.

When the firing temperature is increased to 1000°C, a certain activation of the interaction process takes place in the glaze–ceramics contact zone. It can be seen that a zone of volume interaction appears as a result of unidirectional diffusion of the glaze into the ceramic, which is certainly facilitated by the open porosity. As the same time, the concentrations of the cations Si^{4+} , Al^{3+} , and Ca^{2+} in a small interval (10 μm) in the contact zone become equalized to some extent.

The shape of the concentration curves in the intermediate layer shows that no new reaction products are formed that would differ qualitatively from the initial materials. The Ca^{2+} concentration near the ceramic surface is increased, which can be attributed to the higher degree of crystallization of anorthite at the phase boundary. With an increase in the firing temperature, substantial changes are observed in the distribution of Zr^{4+} . Some of the Zr^{4+} together with the glaze melt migrates into the ceramic, it becomes redistributed inside the glaze coating, and the concentration of Zr^{4+} near the surface increases due to active surface crystallization.

It can be seen in the photomicrograph of the polished section that with increasing temperature the boundary between the ceramics and the glaze becomes less clearly defined, and the intermediate layer formed has a nonuniform thickness, which is related to the inhomogeneity of the chemical composition, grain size, and porosity of the ceramic surface layer. A further increase in the firing temperature to 1050°C intensifies the interaction between the glaze and the ceramics. The photographs clearly exhibit an intermediate zone in the form of a light-colored uneven band (about $40\text{ }\mu\text{m}$). The decrease in the intensity of the typical brownish color can be a result of an increased amount of formed liquid phase in the ceramic substrate, as a consequence of which red-brown iron oxides are dissolved in the glass and lose their chromophoric capacity.

Equalization of the Si^{4+} , Al^{3+} , Ca^{2+} cation concentration and migration of Zr^{4+} extend to a depth of about $40\text{ }\mu\text{m}$. The intense peaks and troughs on the Ca^{2+} concentration curves disappear, which points to dissolution of the formed anorthite in the melt and averaging of the composition. The inhomogeneity of the Zr^{4+} distribution becomes somewhat lower, which can be accounted for by partial passage of it into the melt. This is supported by data of an x-ray phase analysis and electron microscopy.

For the purpose of studying the changes in the structure of the intermediate layer in relation to the duration of the hold in heat treatment, the distribution of the indicated ions in the ceramic substrate and the glaze coating was studied for sample 13 at a firing temperature of 950°C and a hold of 15, 30, and 60 min (Fig. 3). The concentration of the ions in the glaze and the ceramics is different, as in the previous case. The amount of Si^{4+} ions in the glaze remains virtually constant in all the modes of treatment considered, which is not so for the ceramic substrate: the intensity of the silicon ion concentration is unstable due to active crystallization processes in the ceramics at a temperature of 950°C . It is only when the duration of the hold is increased to 60 min that the distribution of these cations becomes averaged somewhat.

The concentration of the Zr^{4+} cations in the ceramic substrate is equal to zero for all the hold values. The Zr^{4+} ions are distributed nonuniformly in the glaze, which is due to the features of the formation of the crystalline phase. The gradual decrease in the intensity of the concentration of the zirconium ions in approaching the formally designated interme-

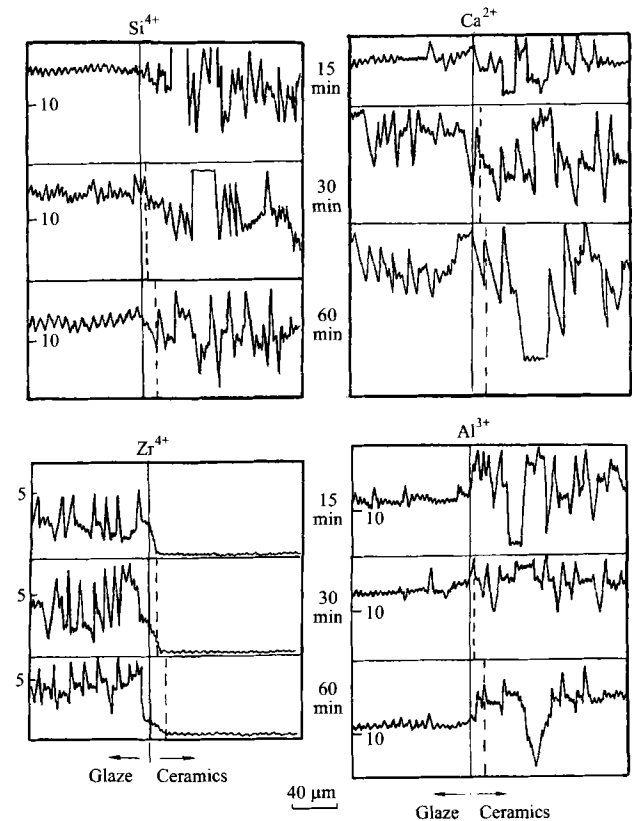


Fig. 3. Cation distribution in the glaze – ceramics system versus firing duration.

mediate zone (approximately $5 - 20\text{ }\mu\text{m}$ thick) points to insignificant migration of these cations into the intermediate zone.

A change in the time parameters of the heat treatment does not have a perceptible effect on the concentration of Al^{3+} , whereas a certain relationship is observed for the calcium cations. Whereas the distribution of Ca^{2+} in the glaze after a 15-min hold is rather uniform, an increase in the duration of the hold to 30 and 60 min immediately causes a redistribution of Ca^{2+} with a shift toward the surface of the fire mirror of the coating, which is evidence of an increased amount of the crystalline phase (anorthite) on the surface, as compared to deeper layers. This is supported by data of an x-ray phase analysis.

Electron-microscopic photographs of the intermediate zone of the glaze – ceramics system (Fig. 4) indicate that the heat-treatment holding duration does not have a perceptible effect on the formation of the contact zone. However, the geometric parameters of the indicated zone are in direct dependence on the holding duration at the maximum temperature. Whereas the glaze – ceramics boundary after a 15-min hold has the shape of a virtually straight line, when the holding duration is increased to 30 and 60 min, the reaction processes become more perceptible, although to a lesser degree than with increasing temperature. However, this does not mean that the intermediate zone is absent in articles sub-

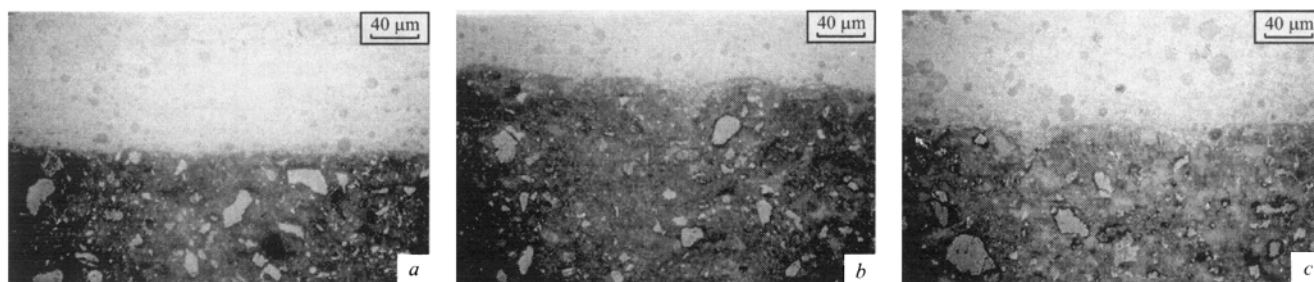


Fig. 4. Formation of the contact zone in the glaze – ceramics system in heat treatment (firing temperature 950°C); a, b, c) firing duration 15, 30, and 60 min, respectively.

jected to accelerated firing. Apparently, its thickness is just very small.

The authors of [6] observed that assuming the rate of element diffusion in the glaze – ceramics contact zone to be constant and not to depend on the firing rate, the intermediate-zone thickness under accelerated firing will be proportional to the hold at the maximum temperature. Firing of tiles in an accelerated mode leads only to sintering of the glaze to the ceramic substrate.

Thus, the interaction of glazes with the ceramic substrate is a complicated and important, although insufficiently investigated process. The degree and the nature of the reaction of glazes with the ceramic substrate depend foremost on the heat-treatment temperature and holding duration and on the structure of the glaze and the ceramics. Diffusion becomes more perceptible with increasing heat-treatment temperature than with increasing hold. However, under the temperature regimes considered (950 – 1050°C), diffusion proceeds primarily due to the glaze glass. In order to increase the activity of diffusion processes, a higher temperature and a longer holding duration are required.

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